

Visualization of Complex Hydrocarbon Reaction Systems

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Abstract

Many hydrocarbon reactions of interest involve either poorly characterized reactants and products and/or large numbers of simultaneous reactions. An important step in understanding the behavior of such systems is to develop quantitative pictures of the feeds and products and the transformations which connect them. The processes for constructing these reaction visualizations is illustrated by examining the construction of a molecular model for coal liquefaction and subsequent conversion to distillate products, and the construction of a video simulation of catalytic petroleum naphtha reforming. New techniques which are permitting advances in these visualizations are discussed.

Introduction

When studying feedstocks such as coal or reactions such as those used in converting petroleum to commercial products one must confront an overabundance of information concerning chemical composition and molecular transformations. The essential features which govern the behavior of a material or process may be lost in the detail. In such cases, the production of a simple picture, or visualization can be important.

Visualizations can have many values including:

- identifying major deficiencies in knowledge
- highlighting the most important aspects of the structure or reaction system which control reaction behavior, and those which are of relatively minor importance
- setting the stage for more quantitative tools such as predictive kinetic models used in process optimization and control
- training
- as a basis of comparison between the composition of similar materials or the reactions of similar feedstocks
- to stimulate discussion creating focus on controversial aspects of the knowledge.

Over the past 15 years, we have been utilizing visualizations to examine several complex reactions systems. In this paper, we provide a review of the process of creating quantitative reaction visualizations and review their use. We will use as examples the construction of models of coal and coal liquefaction and in a video model of catalytic naphtha reforming.

Making a Quantitative Visual Model - Model of Coal and Coal Liquefaction

The first step in assembling a visual model is to collect available information on composition and reactivity. In the case of coal structure, such information includes the proper distribution of elements, element groups, aliphatic and aromatic carbon species, functional groups (oxygen, sulfur and nitrogen), and reactive crosslinks. Knowledge of the reaction chemistry is critical in providing the glue which binds the structures together in a manner which may be used to simulate reaction behavior.

Quantitative reaction models require information on product yields and quality at many stages of reaction, so that the progressive steps in conversion can be illustrated. By assembling composition information on the feedstock and each of the intermediate products, one constructs structures which are consistent with this information at each severity level. The product distribution at the most mild reaction conditions may be used in conjunction with knowledge of the important reaction processes to feedback information to the necessary structures which must be present in the feed to explain the appearance of the products. In the case of mild coal liquefaction, the processes of aliphatic and etheric crosslink cleavage between aromatic centers, the hydrogenation/dehydrogenation and associated hydrogen transfer reactions, and functional group distribution changes (particularly disappearance of reactive oxygen functional groups) have long be attributed to as the primary important reaction paths. A likely representation assumes that the original coal structure contains components similar to those in the products of

mild liquefaction, modified by hydrogen transfer and defunctionalization, and joined by certain reactive crosslinks. In a similar manner, the products and reactions from somewhat more severe processing may be used to imply the structures of the less severe products forming an iterative chain connecting the products of most severe treatment with the structure of the original feed.

To maintain a quantitative picture, the molar quantities of elements, functional groups, aromatics and aliphatics and the like are continuously accounted for throughout the transformation. Choosing the molecular size of the model is also critical - for coal the size of 10000 daltons proved a good compromise. This provided us with a model which was both large enough to represent the variations in product composition which are observed and to include sufficient quantities of crosslinks and functional groups to characterize the feed properly. Larger models required a far more complex task of construction and resulted in a loss of detail in the overall mass. Smaller models would not permit incorporation of product distribution detail and reactivity which are important in liquefaction behavior.

Figures 1 and 2 show models of a subbituminous and a bituminous coal produced in the manner described above. The models are quantitative in terms of the elemental distributions, aromatic and aliphatic components and functional groups as collected from composition and reaction data. The visualizations allow for a quick comparison between the two coals highlighting similarities and differences. Both illustrate a relatively low degree of aromatics condensation (in comparison to heavy crude oils, for instance) and although differences in the distribution of aromatics exist between the two, these features are relatively minor. The role of oxygen in the chemistry of both is apparent: oxygen is prevalent throughout the structure as crosslinks and ring substituents and multiple opportunities for hydrogen bond formation are seen, especially in the bituminous coal. Clearly any consideration of the reactions of these coals without including oxygen would be insufficient. At the time that these models were constructed, very little information was available on the detailed distribution of much of the oxygen, particularly the ether oxygen. Thus the percentage of ether oxygen present in important structural crosslinks, and the nature of non-crosslink ethers is seen as an important uncertainty in coal structure. For both of these coals, sulfur and nitrogen are seen to play relatively unimportant roles (with only a handful of each element in the 10000 dalton model), at least so far as their importance in the overall structure is concerned.

These models are presented in planar form with the intention of allowing for better visualization of the chemical connectivity. In reality, coal is a three-dimensional structure. Recent advances have allowed construction of more sophisticated models utilizing molecular dynamics to provide energy minimized three dimensional structures. Such models are far superior in representing the constraints imposed by spatial and energetic considerations and provide better tools for examination of three dimensional properties such as density and porosity.

Figures 3 and 4 show the progressive conversion of the bituminous coal via donor solvent liquefaction. The reactive crosslinks are disrupted and products of various functionalities, aromaticities and molecular sizes are generated. With more severe processing, both forward and reverse reactions occur leading to both smaller and larger products. Even at relatively severe conditions, these liquefaction products are substantial in molecular size and contain a significant amounts of heteroatom species (particularly oxygen). Figure 5 shows the products from two-stage liquefaction employing a thermal donor solvent stage and a catalytic hydrotreating stage in close sequence. The comparison of figures 4 and 5 provides a rapid visual sense of the advantages of two-stage technology. In contrast to the solvent products, the two-stage products are of far reduced molecular size and dramatically reduced heteroatom content.

Construction of a Model of Catalytic Naphtha Reforming

The process of catalytic naphtha reforming is an essential feature of the production of high quality gasoline components from crude oil. In reforming, a feedstock consisting entirely of hydrocarbons (no heteroatoms) of carbon numbers typically between C6 and C12 are processed over a catalyst (platinum-rhenium on alumina, for instance) to convert species having a low gasoline octane rating to species with improved octane values. The principal desired reactions involve the dehydrogenation of naphthenes and the dehydrocyclization of paraffins to produce aromatic species. Side reactions of cracking, hydrocracking, and isomerization occur with the desired reactions.

Modeling reforming reactions is complex because many species are reacting simultaneously via many potential reaction paths. Unlike liquefaction, the individual species in reforming can be largely identified using relatively straightforward techniques. The difficulty lies in understanding the balance of reactions occurring for each species, the relative contributions of the reactions for the different feed molecules, and in understanding how to control the reaction to provide the highest yields of desired products.

The process of producing a visualization of the reforming reactions involves many of the steps outlined in construction of the coal models: Namely, collecting detailed information on product composition at various levels of reaction severity and iterating back to the prior composition and reaction changes via information on the reaction matrix allow the transformation model to be constructed. Figures 6 and 7 show a quantitative representation of the feed and products from the reforming of an Arabian naphtha. Even for the relatively mild reforming to a product octane of 81, there has been considerable production of aromatic species and conversion of most of the naphthenes. Heavy paraffins have also been converted, substantial hydrogen has been produced and some of the product has been converted to undesired light gases. Relatively few reactions are needed to explain the product distribution shifts, beyond the dominant roles of dehydrogenation, dehydrocyclization and cracking.

For the reforming visualization, we were interested in producing a tool to enhance the training of new operators and engineers involved in commercial reformer operation. We extended our visualization by creating individual 'snapshots' of the composition at various ranges of severity, taking the reactions one group at a time. These snapshots were then assembled using computer drawings and video tape and assembled into a video depicting the entire sequence of reactions. We have found this video visualization can provide an excellent overall feel for the process of reforming in a very short period of time.

Visualizing - the Future.

A number of emerging tools are permitting visualizations to be created with greater ease, high detail, greater accuracy, and with better ability to serve the valuable roles of visualizations outlined above. These tools include:

- Computational tools for representing molecular connectivity permitting construction of models on a computer platform.
- Use of molecular dynamics software to produce energy-minimized three-dimensional structures.
- Use of quantum mechanical simulations to predict reaction pathways from molecular energetics, reducing the need for experimental determinations of reaction paths and rates.
- Monte-Carlo approaches to assembling possible structures from component pieces and for displaying a full range of potential structures from multiple possibilities.
- Advances in compositional capability permitting models of greater molecular detail.

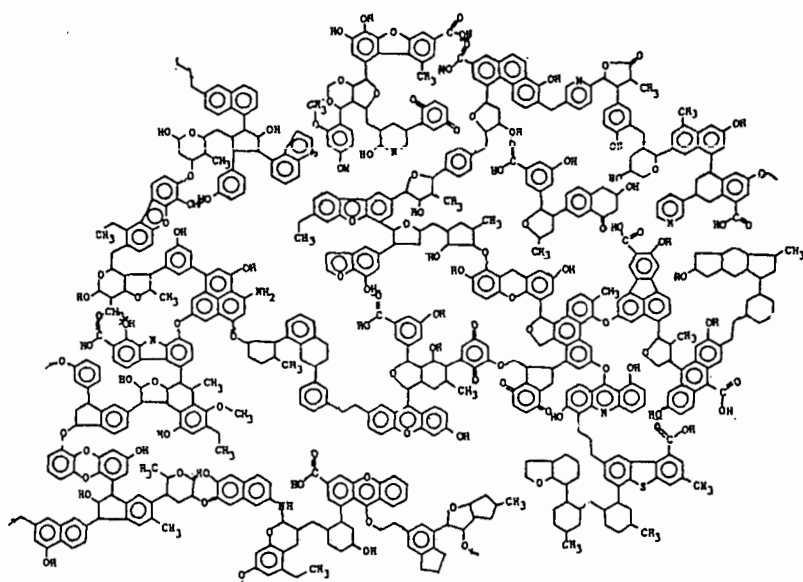


Figure 1. Model of Subbituminous Coal Structure

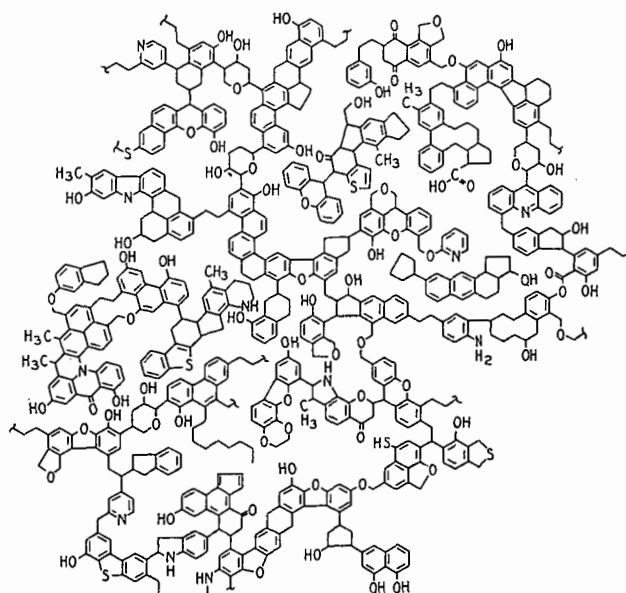


Figure 2. Model of Bituminous Coal Structure.

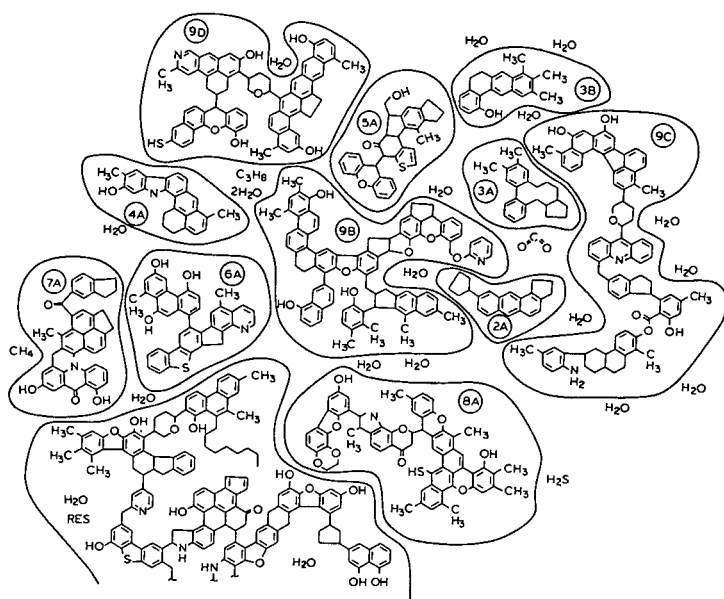


Figure 3. Model of Products from Mild Donor Solvent Liquefaction of Bituminous Coal

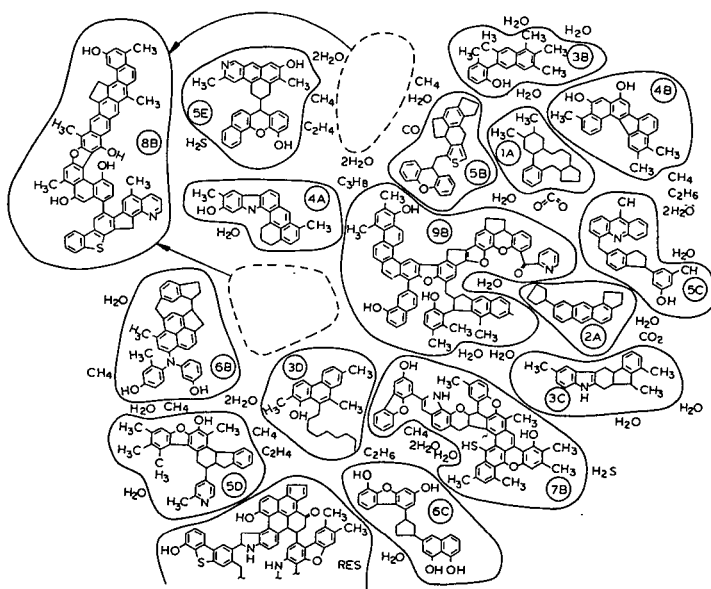


Figure 4. Model of Products from Severe Donor Solvent Liquefaction of Bituminous Coal

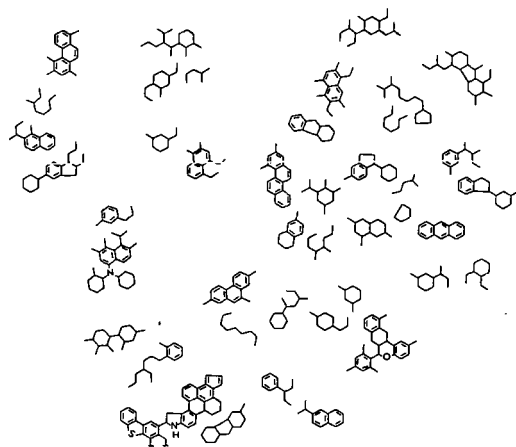


Figure 5. Model of Products from Two-Stage Liquefaction of Bituminous Coal

Arabian Feed Composition		H2		43 RON
Moles per 10000 gm feed		50	100	

Product Distribution		H2		81 RON
Q15321	Q15321	50	100	

Figures 6 and 7. Feed and Products from Mild Reforming of an Arabian Naphtha.

**Feasibility and Status of Coal Gasification
Combined Cycle Plant in JAPAN**

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Keywords: Coal gasifier, Combined cycle, Thermal efficiency

1. Introduction

Integrated Gasification Combined Cycle (IGCC) is regarded as the most powerful candidate for new coal firing power plant in the next generation, because of the following two points: it has a significantly high net thermal efficiency of 46-50+% which can be achieved by increasing the gas turbine inlet temperature, and it maintains superior environmental performance attained by means of a conversion process from "dirty" coal to "clean" purified gas and the disposal of glassy slag ash.

IGCC R&D in JAPAN is being carried out as a part of the "Sunshine Project", a national project concerned with promoting the use of new energies. The Ministry of International Trade and Industry (MITI) had started the IGCC R&D project in 1974, to focus on a fluidized bed coal gasifiers. In 1986, MITI commissioned the New Energy and Industrial Technology Development Organization (NEDO) to restart an IGCC R&D project using an air blown entrained bed coal gasifier at the NAKOSO 200 ton/day pilot plant, the overall project schedule is shown in Figure 1.

This project, now in its final stage of the test operation, was in 1991 entrusted to the IGC Research Association by NEDO. The essential technologies for IGCC have been verified at this pilot plant through the achievement of a month of stable and continuous operation in March, 1995.

This air blown entrained bed gasification concept is more suitable for power generation as compared to the oxygen blown ones developed mainly for chemical plants in Europe and the USA, air blown ones do not require large amounts of the auxiliary power to produce oxygen (See Table 1). However, the air blown entrained bed gasification had several faults to its operation and was, therefore, never successful until our first success in April, 1995.

Due to its successful results, Mitsubishi has newly designed an IGCC system, "THE IGCC system", which provides the highest net thermal plant efficiency and environmental benign in a cost-effective manner.

2. Results of the 200 ton/day air blown entrained bed coal gasification pilot plant operation

2.1 Outline of the 200 ton/day pilot plant

A schematic diagram of the pilot plant's system is shown in Figure 2. This plant, mainly consists of the air blown gasifier (gasifying 200 ton/day of coal), the hot and dry gas clean-up unit and the low calorific coal gas fired gas turbine (12.5MWe of capacity). The gas turbine can be tested and the performance, operational flexibility, reliability, and durability of the air blown IGCC technologies can be verified. Dry gas clean-up is composed of two parallel systems, one is a granular bed gas filter and fluidized bed desulfurization system, and the other is a candle ceramic filter and fixed bed honeycomb desulfurization system. MHI is in charge of supplying the air blown 200 ton/day gasifier, the fixed bed hot and dry gas clean-up unit and the testing stand for the full pressure and full scale gas turbine combustor.

MHI's fixed bed hot and dry gas clean-up unit is composed of a dust removal system made of a porous ceramic filter and honeycomb shaped stationary oxidized iron desulfurization unit. This system is of a significantly compact size and is completely water free. Its superior clean-up performance under high gas temperature conditions of 350~450°C enables the effective use of sensitive heat from coal gas to be used as the gas turbine heat input. The handling system including valves, pipes and controls have been greatly simplified, as there are no moving materials, increasing system reliability and economy. As of September 1995, the accumulative operating hours of the gasifier and the fixed bed clean-up exceeded 3800 hours and 1200 hours respectively, including the one month continuous operation of 789 hours.

It has successfully performed with the satisfactory results. The testing at the pilot plant will be completed by the end of March, 1996.

2.2 Results of the One Month Reliability Test

The 200 ton/day gasifier had achieved one month of continuous operation totaling 789 hours (about 33 days) from 3rd March to 5th April 1995. During this test period, the operation of the gasifier had been continuously stable, and the testing was completed according to the planned schedule. Table 2 shows the major operating parameters of the gasifier during this test.

It was confirmed that the gasifier can maintain sufficiently high heating values to produce coal gas for stable combustion in the gas turbine and also keep discharging continuously molten slag through the slag hole with 100% recycling of char.

Collected data shows superior performance of air blown gasification. 70% of cold gas efficiency, 99.9% of carbon conversion efficiency were obtained, and passes the highest net thermal plant efficiency at any demonstration plant. All of the ash in the coal fed to the gasifier is converted to non-leaching and compact glassy slag with negligible small unreacted carbon, thus enabling simple ash handling and economical ash disposal without fly ash, including unreacted carbon.

The fixed bed gas clean up test facility of a size of 20 ton/day had also achieved 765 hours of continuous operation during the same period of the long term reliability test operation as the 200 ton/day gasifier. This test shows 1~5 mg/Nm³ of dust concentration and 20~50 ppm of sulfur content (H₂S, COS) at the outlet of the clean-up and the durability of the ceramic filter element, the oxidized iron desulfurization agent and the whole system.

Instead of elemental sulfur recovery system, gypsum recovery system under pressurized condition had been tested in the pilot plant.

Another advantage of this fixed bed clean-up equipment is the easiness to scale-up its capacity, because of the simple scale up criteria that requires that only the quantity of the element to be increased in accordance with the gas flow.

4. Mitsubishi IGCC system(THE IGCC system)

Based on the successful results of the 200 ton/day pilot plant, the base data for scaling-up to a 2000 ton/day class demonstration plant were able to be achieved.

The IGCC may be a more complicated system when compared to conventional fossil plants, so system integration and simplification is very important. Since MHI can supply all the key components of IGCC, MHI can drastically simplify the system based on an optimized integration among the interdependent main component and under a single responsibility. The feasibility study on THE IGCC system has been executed, and details its superior performance and economical feasibility.

THE IGCC system is composed of the air blown two stage gasifier , the fixed bed dry gas

clean-up unit and the 1300°C or 1500°C class gas turbine, 701F or 701G (for 50 Hz use) and 501F or 501G (for 60 Hz use).

Adopting the fixed bed gas clean-up system, which is very compact in size and water-free, contributes to the simplicity of the whole plant system and a significant reduction of plant area. The small sized air separation unit (ASU) is installed in order to produce nitrogen as an inert gas for pressurized coal/char handling and seal gas at the gasifier. The remaining oxygen at ASU is mixed with air in the gasifier, so that the oxygen concentration in the gasifier will be 25 vol%.

The predicted performance data is indicated in Table 3.

The net thermal efficiency of THE IGCC system is predicted to be 46~50+ LHV% It achieves a 20% reduction in the CO₂ gas emission with super critical steam condition compared with conventional pulverized coal firing power plants.

The SO_x/NO_x emission at the stack inlet is anticipated to be 10 ppm and the dust concentration is predicted to be less than 1 mg/Nm³ at the inlet of the stack.

MHI is also ready to supply large capacity coal gas fired gas turbines. MHI has the proven technologies of the 1300°C class natural gas fired gas turbines, the 1250 °C class blast furnace gas (BFG gas) fired gas turbines and is presently designing the 1500°C class natural gas firing gas turbines.

MHI has also conducted coal gas firing test with the full pressure and full scale test stand of a gas turbine combustor at the 200 ton/day pilot plant. Its capacity corresponds to one can of the gas turbine for utility use. This test shows stable combustion at a low NO_x conversion rate of 30~40 % (at 1000ppm of NH₃), which is required for the combustion of ammonia rich coal gas.

The gasifier and the gas clean-up unit can be arranged in a single steel structure. The required plant area per power output is reduced by 20% in comparison with conventional coal fired power plants.

The capital cost estimation of THE IGCC system executed at the feasibility study predicts 95% at the commercial phase when compared to conventional coal fired power plants. Consequently, THE IGCC system offers economical feasibility in the generation cost equivalent to that of the existing coal fired power plant.

5. Conclusion

The successful results of the R&D at the 200 ton/day pilot plant have verified the IGCC technologies of the air blown two stage coal gasifier and the fixed bed gas clean-up. The development of air blown IGCC has stepped up to the demonstration phase. The Mitsubishi IGCC system, composed of these technologies, is able to realize the highest net thermal efficiency and environmental benign in a cost-effective manner.

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TYPE	Gasifying Agent		Coal Feed		Gas Clean-up		Thermal Efficiency
	Air	Oxygen	Dry	Wet	Dry	Wet	
NEDO/IGC/MHI	○		○		○		High
Oxygen Blown Type A		○	○			○	Medium
Oxygen Blown Type B		○		○		○	Medium

Table 1 Comparison of IGCC System

	Unit	Plan	Result
Coal Gas Calorie (HHV)	kJ/m ³ N	4,150	4,200~4,600
Coal Gas Flow	T/hr	50.2(at 100%LOAD)	40(75%)~50(100%)
Sulfur Concentration (Inlet)	ppm	<1,500	570~670
Sulfur Concentration (Outlet)	ppm	<100	20~50
Dust Concentration (Inlet)	mg/ m ³ N	<3,000	180~230
Dust Concentration (Outlet)	mg/ m ³ N	<10	~1.1

Table 2 One Month Continuous Operation Data of the Pilot Plant

	Unit	Demonstration Plant		Commercial Plant	
Target	year	2000		2010	
Cycle	Hz	50	60	50	60
Gasifier	-	Air Blown Two Stage Entrained Bed Type			
Capacity	t/day	2,400	1,700	3,100	2,300
Dust Removal	-	Porous Ceramic Filter Type			
Desulfurization	-	Honeycomb Fixed Bed Type			
Gas Turbine	-	701F	501F	701G	501G
Gross Output	MW	400	275	546	408
Net Output	MW	368	255	510	380
Gross Efficiency	% LHV	46	46	50	50
SOx/NOx Emission	ppm	10/10			
Dust Emission	mg/m ³ N	1			

Table 3 Major Specification of THE IGCC system

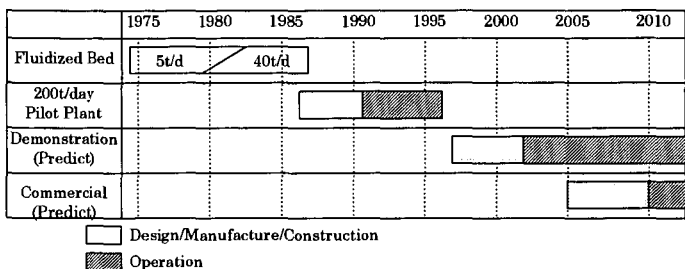


Figure 1 Master Schedule of IGCC Project in JAPAN

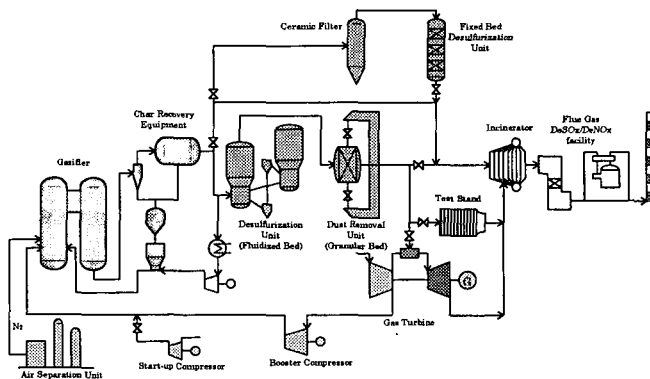


Figure 2 System Flow Diagram of 200ton/day pilot plant

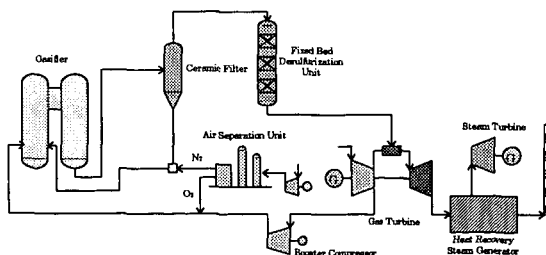


Figure 3 System Flow Diagram of THE IGCC plant

COKING PROBLEMS ASSOCIATED WITH HYDROCARBON CONVERSION PROCESSES

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Keywords: coke formation, coke mitigation, catalytic carbon, metal catalysts

ABSTRACT

The understanding of the factors controlling the deposition of carbonaceous solids resulting from the decomposition of hydrocarbons over hot metal surfaces has a considerable impact on a number of commercial processes including, catalytic steam reforming of methane, steam cracking of paraffinic feed stocks and systems involving carbon monoxide disproportionation reactions. The potential for carbon formation exists in any system in which hydrocarbons undergo thermal decomposition and it is well known that certain metals can increase the overall rate of this process by catalyzing the growth of filamentous and graphitic types of deposit. The highest catalytic activity for carbon deposition is exhibited by iron, cobalt and nickel, and alloys containing these metals. In this paper a review of the information obtained from the use of a combination of controlled atmosphere and high resolution transmission electron microscopy techniques to study the dynamics of carbon deposition arising from the metal catalyzed decomposition of hydrocarbons will be presented.

INTRODUCTION

A number of review articles have highlighted the complex nature of carbon deposits produced during hydrocarbon decomposition reactions (1-6). The major constituents of a typical carbonaceous solid that might accumulate on a metal surface, either in the form of a tube or as a particle dispersed on a support medium, can be divided into three main classes: amorphous, filamentous and graphitic platelets. During a traditional routine analysis of a contaminated reactor vessel or a spent catalyst, these three forms of carbon would not be necessarily distinguished, but merely referred to collectively as "coke". Available evidence indicates that the amorphous carbon component is formed via condensation and polymerization reactions and this material originates from thermal processes. It is conceivable that a significant amount of hydrogen is incorporated in the deposit, however, as the temperature is raised dehydrogenation reactions will tend to reduce the hydrogen content. There is now a general consensus that the formation of the filamentous and graphitic forms of carbon require the participation of a catalytic entity that usually operates in a particulate form.

The mechanism commonly accepted to account for the observed characteristics of the steady-state growth of carbon filaments from the metal catalyzed decomposition of carbon-containing gases involves the following steps (7-9):

- (a) adsorption of reactant gas molecules at particular faces of the metal particle followed by decomposition to generate carbon species, and
- (b) dissolution in and diffusion of carbon species through the metal particle to a different set of faces that favor precipitation of carbon in the form of a fibrous structure.

The latter set of faces control not only the degree of crystalline perfection of the deposited carbon filament, but also the conformational characteristics of the material. A consequence of this phenomenon is that certain metal faces will remain free of deposited carbon and therefore, available for continued reaction with the hydrocarbon.

While the rudiments of the formation of the graphite platelet deposit have not received the same attention as that devoted to the growth of filamentous carbon it is probable that many of the steps outlined above are also operative in the formation of this type of carbon. Nolan and coworkers (10) reported that graphite, in the form of a shell structure surrounding a metal particle core, was the exclusive type of deposit produced from a carbon monoxide reactant containing no added hydrogen. They observed that the limiting thickness of the graphite shells was about 30 layers, and that this parameter was dependent on the lifetime of the metal catalyst particles. Based on these findings, they argued that the growth of graphite layers did not occur via a mechanism that involved precipitation of carbon from the surface of the metal. These claims were in direct conflict those of earlier studies (11-13) that clearly demonstrated that precipitation was the key step in the formation of graphite.

CHARACTERIZATION OF CARBON DEPOSITS

Before proceeding further it is worthwhile to consider the relative rates of the formation of these three types of carbon as a function of reaction temperature and the plot, Figure 1 provides an indication of the typical composition of the "coke deposit" that one might

expect under various conditions from the interaction of a metal with a hydrocarbon environment. It can be seen that for reactions conducted between 400 to 650°C, the composition of the deposit will tend to consist of a large fraction of filamentous carbon and when such reactions are allowed to proceed for a prolonged period of time the fibrous structures will undergo a thickening process due to the accumulation of an amorphous carbon coating. A further ramification of this sequence of events is that the growth of filamentous carbon on a reactor tube wall provides a high surface collection site for trapping the amorphous carbon constituent and this combination effectively produces a very strong composite material. At temperatures in excess of 750°C the contribution of carbon filaments to the overall deposit will tend to decline while that of amorphous carbon will exhibit a steady increase and the emergence of the graphite platelet constituent will become evident.

The details of the growth kinetic aspects of individual carbon filaments was elucidated a number of years ago from quantitative analysis of the dynamic events captured on videotape from experiments performed in the controlled atmosphere electron microscope. From measurements of the rate of increase in length of similar width structures as a function of temperature it was possible to evaluate apparent activation energies for the growth of filaments from various metal catalysts. The important aspect to emerge from this exercise was that from the accumulated data Baker and coworkers (7) were able to develop a mechanism that accounted for several of the growth characteristics and also established that the rate controlling step in the process was carbon diffusion through the catalyst particle. In more recent years (14-17) it has been recognized that the structural perfection of the deposited carbon solid is a parameter that is governed by the nature and shape of the catalyst particle and crystallographic orientation of the precipitating faces as shown schematically in Figure 2a-2c. In addition, symmetrical diffusion of carbon species through the particle will give rise to a relatively straight structure. In contrast, when certain additives are present in the metal particle the diffusion characteristics are modified and this factor causes a non-balanced process that results in the formation of coiled structures.

METHODS OF INHIBITING CATALYTIC CARBON FORMATION

The realization that the chemical and physical nature of metal particles plays a key role in catalyzing the growth of the filamentous form of carbon and that this material is also responsible for providing a very efficient method of trapping other types of deposit has lead to a number of approaches designed to inhibit its formation. These methods have tended to fall into the categories of either coating treatments of the metal surface with inert materials or the addition of selected compounds to the gas phase that might be expected to poison the activity of the metal towards catalytic carbon formation. From a consideration of the investigations that have been carried out, it is possible to establish a classification for the roles of various additives on the inhibition of filamentous carbon growth (18).

- (a) There are some materials that merely provide a physical barrier towards hydrocarbon adsorption and subsequent decomposition on the metal surface, but during repeated temperature cycling tend to spall and the coating loses its effectiveness. e.g. Al_2O_3 , B_2O_3
- (b) Other additives reduce carbon solubility in the metal catalyst, but have no effect on the carbon diffusion characteristics through the particle, e.g. MoO_3 , WO_3 and Ta_2O_5
- (c) There are cases where an additive can reduce both the solubility of carbon and its diffusion through the metal particles, e.g. SiO_2 , and finally,
- (d) There certain electro-negative elements that when introduced into the either as a pre-treatment or on a continuous basis, effectively modify the chemistry of the metal surface so that it can no longer function as a catalyst to dissociatively chemisorb the carbon-containing gas molecules, e.g. sulfur, phosphorus and halides.

ISSUES THAT NEED TO BE ADDRESSED WITH REGARD TO CATALYTIC CARBON DEPOSITION

When one examines the ramifications of filamentous carbon formation under conditions where such structures are produced on either a metal tube surface or on isolated metal particles supported on a carrier material there are a number of questions that at point in time have not been satisfactorily answered. It is not clear whether these fibrous structures merely function as a high surface collection site or if they perform a catalytic function in being able to promote the formation of amorphous carbon from interaction with gas phase reactants. One might also offer a counter argument that an enhancement in the formation of the amorphous carbon component could effectively form a physically blockage of the metal surface, thereby inhibiting its catalytic action with respect to growth of filamentous carbon. A further factor could have a significant impact on the particular hydrocarbon conversion process is the possible impact of the fibrous material on the mass flow of reactants under either gas or liquid phase conditions.

Other potential problems center around the identity and fate of metal particles that perform the catalytic function. While we have established which metals are the most catalytically active for the growth of filamentous carbon there are still unsolved mysteries surrounding the precise influence of small amounts of a second metal. The addition of very small amounts of silver, tin, or copper to nickel, iron or cobalt can result in a dramatic increase in the ability of the ferromagnetic metal to catalyze the growth of filamentous carbon. Under a typical commercial reactor condition one must be aware that the likelihood of introducing impurity species into a host metal is extremely high and this behavior could have catastrophic effects on the carbon deposition process. Finally, it is imperative that we are able to determine the influence, if any, of the metallic inclusions in the deposit on the subsequent decoking step. It would be pertinent to ask whether such species function as catalysts for the removal of carbon and under these circumstances what is the fate of the metal particles following the gasification reaction. The ramifications of the difference in behavior of metal particles associated with filamentous carbon during reaction in oxygen is depicted in Figure 3. In the case where the metal facilitates the removal of carbon the particle returns to the original location on the support medium. In contrast, where gasification proceeds without the participation of the metal, then there is a high probability will eventually be swept out of the system by the reactant gas stream. In this context it might be worthwhile in certain reaction systems to consider introducing additives during the decoking cycle that are known to be good catalysts for the carbon gasification step and that are either benign towards carbon deposition or can easily be removed prior to re-introduction of the hydrocarbon feed.

SUMMARY

In conclusion, it is clear that significant improvements have been made over recent years with respect to controlling the rate of carbon deposition in a selected number of systems. There is, however, a strong case to be made for attention to be focused on some of the fundamental aspects of this problem so more effective treatments can be developed. One must be mindful that such treatments may not have universal application and it is necessary to be cognizant of a number of prevailing factors when one is attempting to design an inhibition package for a given system. These aspects include, the nature of the metal surfaces and the reactant molecules, the temperature at which contact between these components will occur and some knowledge of the identity and concentration of possible contaminants that may be present, particularly in the gas phase.

ACKNOWLEDGMENTS

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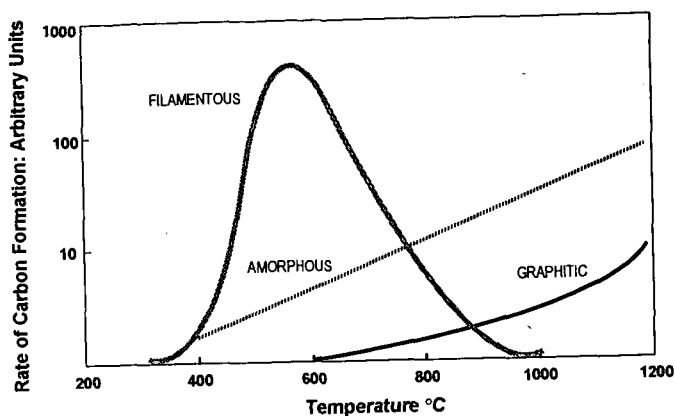


Figure 1. Relative rates of formation of the three types of carbon deposit as a function of reaction T.

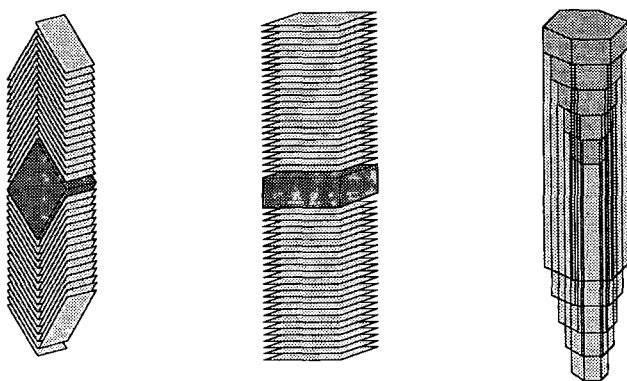


Figure 2. Schematic representation of different types of filamentous carbon structures

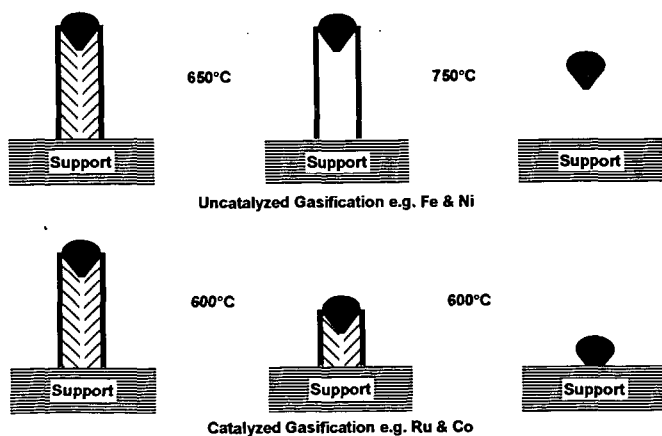


Figure 3. Fates of catalyst particles during gasification of filamentous carbon in O_2

Introduction to Hydrocarbon Conversion Science and Achievements of Professor Isao Mochida

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Background to the studies of I. Mochida

Fossil fuels, such as coal, petroleum and natural gas (methane), although used dominantly as fuels, either by direct combustion, or to power engines, have other significant uses. Coal is carbonized, directly, to produce metallurgical coke and coal-tar from which is derived coal-tar pitch, this material being a precursor to several carbon artifacts. Further, coal can be 'liquefied' to produce acceptable fuels, although the economics for this, currently, are far from favorable. Each of these conversion processes has been studied extensively by Mochida, to produce industrially acceptable materials, and to be able to use, more effectively, raw materials or feedstocks with less and less acceptable specifications, and to improve the overall economy of the conversion processes.

Likewise, it is with petroleum. Crude petroleum is processed by thermal and vacuum distillation, including catalytic systems, to produce a variety of liquid fuels, for gasoline, diesel and aircraft engines, and for space heating. Not all of the barrel can be converted to such high value products. There exists a variety of 'pitch residues' from the conversion processes. Mid-century, these residues would be used either as a fuel, or would be converted to a solid in the so-called 'delayed cokers', the solid 'delayed coke' being itself used as a fuel or disposed of in land-fill operations. Mid-century onwards, after W.W. II, saw a tremendous increase in the use of petroleum, with associated increases in the tonnage of 'pitch residues' which required disposal. However, during this growth process it was realized that these 'pitch residues' could have commercial application, and that their status could be raised to that of a 'by-product'. Thus, the 'delayed coker' became more than a disposal unit, it became specialized equipment to produce the required 'sponge' (or 'regular') cokes and 'needle' cokes. Mochida undertook a massive programme of research into the workings of delayed cokers, and improvements in quality of delayed cokes. Delayed cokes find an irreplaceable use in the manufacture of carbon anodes which are used in the Hall-Héroult cells of the aluminum industry, and the large electrodes of the steel industry, used to transmit electrical energy into the crucibles of steel production.

Personal notes: I. Mochida

Professor Isao Mochida, born in 1944, took his B. Eng. in the University of Tokyo in 1963, with a M. Eng. also from the University of Tokyo, specializing in Linear Free Energy Relationships in Heterogeneous Catalysis. He joined the University of Kyushu in 1968, and currently has the title of Professor: Institute of Advanced Material Study. During these years in Kyushu, Professor Mochida has published 485 Technical Papers, has written 10 Books and has 25 Patents. He spent one year with Professor Harry Marsh, 1977-1978, in the University of Newcastle upon Tyne, U.K. The scientific community has recognized the massive contribution he has already made to the sciences associated with coal and petroleum, and their many derivatives, in the form of eight Awards from Societies both within Japan and abroad. Trained initially in catalysis, he has applied this discipline successfully in his studies associated with carbon science and with coal and petroleum refining. There is more. At the time when relation-

ships between Universities in Japan and Industry needed to be strengthened (and this was a world-wide problem) Mochida worked intensely to build-up a research school, and to relate the findings of this research to the problems which industry was experiencing. Further, this period of time saw a significant growth in the size of research teams from the occasional two or three, to numbers approaching about twenty. And other changes were taking place. These research teams were now including students from outside Japan, and students from Japan were being offered opportunities to study in Universities, worldwide. At the centre of these activities Mochida operated with an apparent limitless energy, with the welfare of his students very much at the fore-front of his thinking. So, simultaneously, massive contributions were made to the sciences of hydrocarbon conversions, and young people were being highly trained to take their place in industrial and academic societies.

New materials: I. Mochida

Mochida has the ability, also, to be extremely innovative. Taking a look at recent issues of the journal *Carbon*, e.g., *Carbon* 1996, Mochida has, with his co-authors, studied the axial nano-scale microstructures in graphitized fibers inherited from liquid crystal mesophase. Limitations to thermal conductance, thermal capacity, tensile strength and Young's modulus of fibre materials, and hence limitations in applications, ultimately depend on the continuity of crystal alignments in such fibres. Such studies are to the fore-front of research into the applications of fibres and are both timely and relevant. Also, Mochida has recently looked at the carbonization properties of the fullerenes C_{60} and C_{70} . Further, in the area of new carbon forms, he has studied the mechanical properties of binderless carbon moulds prepared from heat-treated mesophase pitch of controlled grain size. A similar, but quite distinct problem is that of gas separations. Molecular sieve carbons, similar in behaviour to the microporous zeolites, have been known for some years now. Mochida has applied these approaches to the separation of carbon dioxide from coal-bed methane, a mixture of these two gases, usually heavily contaminated with water vapour. Such a separation requires not only a carbon with the appropriate microporosity, but with this contained between surfaces which are of a hydrophobic nature. The coal-bed methane needs to be of a suitable purity for use in homes and industry.

The mesophase story: I. Mochida

During his career, Mochida has applied his earlier training in catalysis to reactions associated with the formation of carbons, of diverse properties, from various original, aromatic feedstocks. Studies have been published of catalytic syntheses of 'mesophase' pitch from aromatic hydrocarbons, such processes allowing the molecular design of carbon precursors. Synthetic methods have been developed for the creation of pitches from pure aromatic hydrocarbons using such Lewis acids as HF/BF_3 or $AlCl_3$ as catalysts. The preparation of nitrogen-containing pitches, from quinoline and isoquinoline, is an attempt to understand how differences in locations of nitrogen atoms, within the ring structures of the graphene layer of graphitizable carbons, influences the carbonization properties of the starting materials and the properties of the derived carbons.

However, very significant contributions of Mochida are with the conversions of coal and petroleum to carbons and further derived materials. These two sources or feedstocks have two aspects in common. Both are very complex organic materials which require careful structural and chemical analyses, and both, on pyrolysis and carbonization, when in the fluid state, are able to form liquid-crystal systems, that is, the so-called mesophase. In simple terms, there are

many 'mesophases' which give the diverse structures to graphitizable carbons. Mesophases are generated from molecules (mesogens), size $\approx 1,000$ u, formed during carbonizations of coals and pitches. Mesogens, themselves, possess a wide range of chemical reactivity, and it is this variation which results in liquid crystal formation of differing size and ability to coalesce. Herein lies another long story. It is the 'crystallinity' of these liquid-crystals which is carried over into the solid phase of the carbon or coke, and which imparts the associated properties of anisotropy and graphitizability. By way of comparison, if wood material or a phenolic resin is carbonized, without passing through a fluid phase, then the resultant carbon, although not amorphous, is of limited structural order, is isotropic, and certainly is non-graphitizable.

Coal carbonization: I. Mochida

As far as coal is concerned it has to be recognized that 'coal materials' exhibit a wide range of chemical and physical properties, called 'coal rank'. The youngest of coals, the lignites and brown coals, with their internal co-valent bonding, do not fuse on carbonization, but produce carbons (or chars) which are meso- and micro-porous and hence have the properties of an adsorbent. As the rank range is traversed, the co-valent bonding is progressively replaced by hydrogen bonding and Van der Waals bonding, this enabling the coals to fuse on carbonization. The structure of the coal also becomes progressively more aromatic in content. With a further increase in rank, it is found that this fusibility, or softening or plasticity reaches a maximum to descend to zero in the semi-anthracites and anthracites, where the weak hydrogen bonding is replaced by carbon to carbon co-valent bonding. It is the coals with descending fusibility which have coking ability. However, the making of metallurgical coke no longer depends upon the use of a single coal being fed to the coking ovens. Rather, quite often, more than ten coals are previously blended and it is the blend which is charged to the coke ovens to be subsequently carbonized. Each of the ten or more coals, on their own, would not make a metallurgical coke. Procedures involving co-carbonizations of the coal (coal blend) with additives of high solubility parameters and hydrogen transfer ability were developed. It is this theory of the carbonization process, the interactions within the mixed fused states, and the formation of liquid-crystal systems and the fusing of these liquid-crystals, which has enabled the technology of coke-making to advance in the way it has done.

Coal, essentially, and considering the vitrinite macerals, is an organic, macromolecular system, containing microporosity. The ability of the coal to fuse (depolymerize) is a function of the strength of bonding within the macromolecular networks. Pyrolysis of coal produces molecular degradation to form the plastic (liquid) system. Subsequent carbonization brings about dehydrogenative polymerization of the dominantly aromatic molecules within plastic coal such that when the molecular size is about 1,000 u, formation of liquid crystals occurs and coke structure is established. Depolymerization of higher activation energies is favoured at higher temperatures, with rapid heating to prevent the retrogressive reactions at lower temperatures. Rapid heating under pressure is favorable with the use of additives in co-carbonizations because they have an enhanced facility for dissolution in the coal and reaction at higher temperatures. Mochida has submitted a proposal to the Ministry of International Trade and Industry and Japanese Association of Iron and Steel Making, which outlines coke-making procedures to be adopted in the next decade. The proposal includes coal pretreatment, rapid heating to enhance the fusibility for coke strength, by lower temperature of calcination, and potential for anisotropic development, hot moulding, and carbonization at controlled heating rates. The application of such a scheme would widen the range of usable coals, would make coke making less energy intensive, improving quality and productivity, and suggesting the possibility of a continuous rather than a batch process of coke making.

Coal liquefaction: I. Mochida

A thorough understanding of the macromolecular structures of coal, of bondings within and between these macromolecules, as well as the microporosity (so enabling reactive molecules to enter into coal structure) has enabled Mochida to improve the process of coal liquefaction. Early on, he demonstrated the importance of coal liquefaction solvents in terms of their boiling range, their dissolving ability and capacity as well as the reactivity of hydrogen donating molecules. Hydrogen donors not only stabilize radicals from coal pyrolysis but also lead to bond fissure of the rather more stable bridges, so achieving larger extents of depolymerization and hence of oil yield. In the area of liquefaction catalysts, the contribution of Mochida is with the design, the recovery and regeneration of catalysts, proposing the use of TiO_2 and carbon. He has advanced integrated schemes which include coal pretreatment, coal dissolution using donors at high temperatures, with two or three steps for the catalytic upgrading, such as hydro-desulfurization and hydro-denitrification.

Activated cokes (carbons): I. Mochida

Professor Mochida applied his combined understanding of coal chemistry and structure, as well as surface chemistry and heterogeneous catalysis to the production of activated carbons from coal, with the viewpoint of efficient removal of oxides of nitrogen and sulfur from combustion gases. Using a bituminous coal, he produced an activated carbon of higher performance characteristics than that of Bergbau Forschung (now DMT). He found (a) that the activity of the carbon for NO_x reduction, using ammonia, is intimately related to the oxygen functionality associated with the oxidatively adsorbed SO_2 , (b) that nitrogen functional groups introduced into the carbon, during the stage of the $\text{NH}_3\text{-NO}$ reaction, enhance the NO_x reduction, and (c) that the regeneration of SO_2 adsorption activity, after SO_2 recovery, relates to extents of surface oxygen complexes contained on carbon surfaces. Removal of SO_x and NO_x using activated coke (from coal) is now commercialized in Japan. The same principles have been applied to activated carbon fibers from PAN (polyacrylonitrile).

TECHNOLOGICAL DEVELOPMENT IN THE COAL AND HEAVY PETROLEUM UP-GRADING TO FUTURE SOCIETY

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INTRODUCTION

Energy basically obtained from the fossil carbonaceous resources on the earth will suffer the shortage of supply principally due to rapidly growing demand in the developing countries of large population. Huge consumption of the resources will bring about significant damages to the global environment. Hence, extensive up-grading of petroleum and coal at very high efficiency, energy saving, and environmental protection should be pursued at the same time. The correct structure of fossil resources, molecular transformation of their complete conversion and reforming by multi-stage scheme, catalysis and catalyst designs for the respective stage, molecular transformation into the carbon of high performances for energy saving and environmental protection are the targets of current research.

In the present paper, concepts and results in such areas that have been studied by the author for 20 years are overviewed.

Structural Understanding of Coal and Petroleum

Coal and petroleum are both complex mixtures of hydrocarbons. Their heaviest ends are targets of detail structural analyses.

Coal has been characterized by its maceral compositions and ranks, which tell us empirical but useful correlations on its properties. Recent approach is to clarify its structure on molecular basis. Basically heavy molecules in the coal are polynuclear polyaromatic hydrocarbons with heteroatoms and alkyl substituents. Sizes of molecule and aromatic ring, number of nuclei, bindings among nuclei, moiety of heteroatoms, number and length of alkyl substituents are primary factors of molecules. The distribution of the factors is concerned while the molecular weight is estimated around 1500. Such macromolecular chains are entangled each other to form colloid or micelle which occludes smaller molecules. The bridges among the chains can be covalent or non-covalent. Recent study indicates that non-covalent bonds among the chains are breakable rather easily by physical as well as chemical pretreatment at least in active macerals, providing high solubility and fusibility after the liberation. Non-covalent bridges are hydrogen bond, charge transfer interaction, aromatic ring stacking and metallic ion bridges. The author emphasized the carboxyl linkage and their coordination to divalent cations in lower ranking coals as shown in Figure 1. Although the complete picture of coal molecules is not disclosed yet, analysis based on such a profile of molecules gives us an image of its chemical nature.

The asphaltene is another target of structural study, while the molecules in naphtha, gas oil, vacuum gas oil and maltene are fairly clarified, their accuracy depending on their molecular size and type of structure. The asphaltene is soluble in benzene, but is believed to be present in the micelle or an entangled assembly, molecular weight of the component being beyond 10,000. Molecular assembly of the asphaltene in vacuum residue should be clarified at elevated and ambient temperatures. The present authors have hydrogenated 99% of hexane insoluble component into hexane soluble. Interestingly, solubilized asphaltene inherits the basic metal porphyrin structures. Structural change at this solubilization gives us some keys to elucidate the molecular assembly in the asphaltene.

Molecular Transformation of Coal and Heavy Petroleum

When coal and heavy fraction of asphaltene are heated, their molecular assembly is to be liberated to give a fused state from coal and solution from the asphaltene. Solvent present or added plays an important role to produce such a liquid state. In another situation without adequate solvent or with strong intermolecular linkages, condensation reactions of macromolecules can take place within the cage of molecular assembly, giving less soluble and less fusible component. Hence, the decaugulation of molecular assembly prior to the heating is claimed by the author very favorable to suppress such retrogressive reactions. The condensed product, thus produced, is called char or isotropic carbon with least stacking of aromatic planes. The author emphasizes the importance of hydrogen donor and dissolving activity of the solvent.

The polymeric substances in the liquid state can be depolymerized through the breakage of the weakest intermolecular linkages. Such breakage can be spontaneous, hydrogenation assisted, and hydrogenolysis as schematically illustrated in Figure 2. The fissured linkage can be capped with hydrogen to give smaller molecules, otherwise another type of condensation reaction takes place to give large molecule of more stability, leading to carbonaceous product. Such a process can be defined as carbonization or coking, being a principle pathway to produce carbon materials of functionality or process-troubles such as sludge, plugging and carbonaceous poisons as described later. Competitive reaction scheme is illustrated in Figure 3. Hydrogenation-assisted and hydrogenolysis breakages are performed with hydrogen donors at rather high temperature and rapid heating.

The limitation in such mechanisms of depolymerization is certainly present in the reactivities of acceptors and donors, limiting the extent of depolymerization. The catalyst can

perform further depolymerization through the hydrogenation, acidic and hydro-cracking to give distillates.

Catalysis and Catalyst Design for the Molecular Conversion

The catalysts can hydrogenate the aromatic ring and break the single C-C, C-S, C-N, C-O bonds due to their hydrogenation activity originating from transition metal components and their acidity. The hydrogenation produces hydrogen donor, caps the free radical, and saturates the double bonds to be fissured by acidity. The aromatic ring can be opened into chain molecule through the successive steps of hydrogenation and acidic bond fission. Alkylation and trans-alkylation modify the nature of aromatic species.

The hydrogenation can suppress the retrogressive and coking reactions though the control of condensation reactions and enhancing fusibility or solubility. On the other hand, acidity of the catalyst adsorbs strongly the polar molecules, trapping them on the surface for a long time while the condensation reaction takes place consecutively, leading to the carbon or coke on the catalyst surface.

Demetallation, desulfurization, denitrogenation and deoxygenation are major catalytic reactions for up-grading the hydrocarbon fuels. The molecular conversions pathways involved in the reactions are now being schematically described, although the difficulty increases with increasing molecular size because of difficulty in their molecular identification.

Another important factor is the intermolecular interactions in the liquid phase and on the catalyst surface. In some combinations, such interaction enhances the reaction while retards the reaction in other cases. Desulfurization of gas oil has been described on molecular bases. Chemistry involved in the desulfurization of 4,6-dimethyldibenzothiophene has been clarified.

The catalysts of better performances such as longer life, easy recovery and regeneration as well as high activity and selectivity are continuously looked for. The catalytic species and support are combined to achieve high performance, their chemical as well as physical interactions being concerned. Carbon and titania are reported to provide non-polar surface of intimate interaction with the catalytic species. Very fine particles of carbon as photographed in **Figure 4** are well dispersed and recoverable from ash minerals. New materials and new combinations are examined to obtain multi-functions.

The catalysis schemes are designed to allow the best performances of the catalysts. Optimum conditions are present to the optimum feed on the respective catalyst. Multi-stage reaction scheme is thus appropriate for the complete and selective conversion of coal and heavy petroleum, selecting the best catalyst and conditions for the respective stage. Solvent plays an important role even in the catalytic reactions.

Molecular Conversion of Coal and Heavy Petroleum into Carbons of High Performances

Carbons produced from coal and heavy petroleum are very indispensable by their high performances in the modern industry. Blast furnace coke, needle coke, carbon fiber and a variety of carbon artifacts are the case. Majority of such carbons is graphitizable through the ordered stacking of aromatic planes which is built in the early stage of carbonization. The mesophase or discotic liquid crystal is the intermediate state and product, leading to such carbons.

It is emphasized that the condensation into large aromatic planes and their stacking are balanced by selecting the feed, additive, preparative conditions and even catalysts of easy separation to form the mesophase. The author particularly emphasized roles of additives of hydrogen donating and dissolving activity. Molecular structure and molecular assembly at micro-, meso- and macro-scopic levels have been analyzed, and their relation to their properties is established. **Figure 5** illustrates microscopic views of mesophase, its as-spun and carbonized fibers. Thus, the carbons of high performance are designed through the preparation of precursor, and control of carbonization, graphitization, and forming on chemical and physical bases.

Carbon Materials for Energy Saving and Environmental Protection

The energy saving and environmental protection are the key issues for the effective use of resources. Carbon can provide some of excellent devices for these purposes. High strength per weight, high thermal conductivity, rapid and large adsorption and desorption, catalytically active surface of carbon fiber and active carbon fibers are such cases. Detail structural control for aromatic molecules including substituents and heteroatoms, and their stacking is the base for the design of the mesophase pitch and hence its derived high performance carbons. Very high strength and thermal conductivity are now achieved from aromatic hydrocarbon derived mesophase pitches prepared with HF/BF₃.

The author proposed a novel scheme of SO_x and NO_x removal over activated carbon fibers of controlled surface as shown in **Figure 6**. The calcination after the activation was found very effective to increase the activity for SO_x oxidation and NO_x reduction.

The authors are very grateful to all of his colleagues and many students at Kyushu University, a number of friends in the academics and industries of international linkages for their significant cowork and helps, and expresses special thanks to Professors Kenjiro Takeshita, Tetsuro Seiyama, Yukio Yoneda, John C. Bailar Jr., and Harry Marsh for their continuous guidance and friendship for many years of his research.

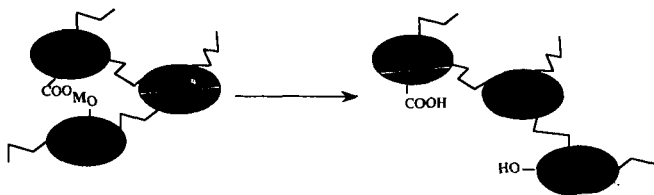


Figure 1 Coal Depolymerization Scheme through Decationing Treatment

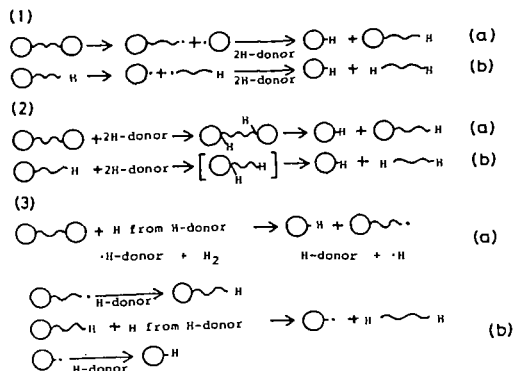


Fig.2 Hydrogen-transferring liquefaction mechanism
 (1) Hydrogenative stabilization of fragmental radicals
 (2) Hydrogenative bond-loosening
 (3) Hydrogenative bond-dissociation
 (molecular hydrogen participation)

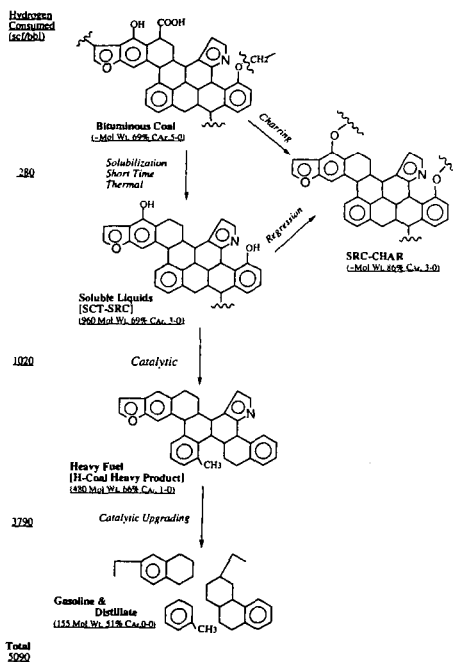


Figure 3 Structural Changes During Coal Liquefaction

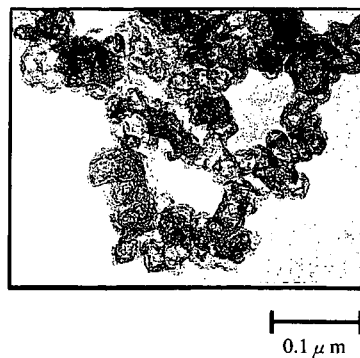


Figure 4 TEM photomicrograph of Ketjen Black

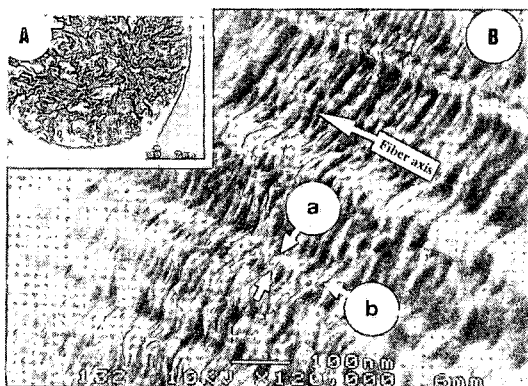


Figure 5 HR-SEM of mesophase pitch carbon fiber

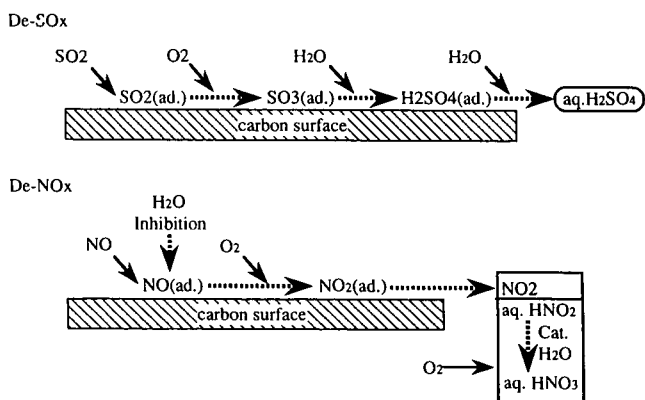


Figure 6 A Novel Scheme of SO_x and NO_x Removal over ACF